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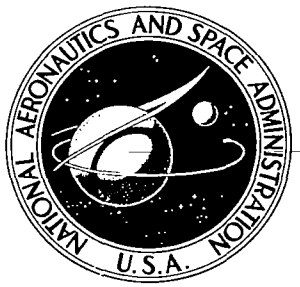

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ELEVATED TEMPERATURE INSTABILITY OF STELLITE 6B

by H. Derow and H. E. Bleil

Prepared by
AEROJET-GENERAL CORPORATION
Azusa, Calif.
for Lewis Research Center

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16. Abstract

A series of studies was conducted to evaluate Stellite 6B as a material for aerodynamic parts in the SNAP-8 mercury turbine. These studies were initiated as the result of a premature, brittle-type failure of components during a SNAP-8 mercury turbine test. The studies included the determination of the metallurgical effects caused by elevated temperature exposure and the resultant change in the material's properties. Additional studies were conducted to establish trends in the effect of material processing on the stability of Stellite 6B and to evaluate the potential for rendering the material stable against the elevated temperature reaction. This report covers the studies, the test procedures, and a summary of the test results.

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FOREWORD

The work described in this report was performed by Aerojet-General Corporation, Azusa, California, under NASA contract NAS 5-417 with W. F. Banks, of the Aerojet Power Systems Department, as the Aerojet-General Corporation Project Manager and M. J. Saari, of the Lewis Research Center Space Power Systems Division, as the NASA Project Manager. The report was originally issued as Aerojet report 3659.

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SUMMARY

SNAP-8 mercury turbines accumulated over 1000 hours operation with Stellite 6B aerodynamic parts exposed at 700° to 1250°F to mercury vapor of varying quality from approximately 75% quality to superheated vapor. Mercury erosion did not occur, supporting the previously established erosion resistance of the material, however, a premature, brittle type of failure of several components did occur. Metallurgical analysis revealed that the Stellite 6B components which failed, had undergone an unanticipated and previously unreported hardening and crystal structure change during the SNAP-8 system operation. These metallurgical changes resulted in a marked decrease in the ductility of the alloy which in turn led to catastrophic failure.

Metallographic and analytical chemistry studies were conducted using the techniques of microscopic examination, X-ray diffraction and electron microprobe analysis to evaluate the effects of the elevated temperature instability on the various crystallographic constituents of Stellite 6B. For material solution annealed at 2250°F and air cooled, a reaction occurred within the temperature range studied, 700° to 1550°F. This increased the hardness of the material; tended to transform the microstructure from face centered cubic (FCC) to hexagonal close packed (HCP); and transformed the normal M_7C_3 carbide islands in the matrix to $M_{23}C_6$.

Change in the Stellite 6B matrix from FCC to HCP, a more densely packed atomic crystal structure, causes a linear contraction of 0.092%. A statistical analysis of the data established a standard deviation in this figure of ± 0.042%.

The mechanical properties of Stellite 6B were determined in both the solution annealed, unexposed and elevated temperature exposed conditions. The results indicated that the elevated temperature reaction severely reduces the ductility and impact properties and moderately reduces the tensile yield strength but does not detrimentally affect the ultimate tensile strength. The reduced ductility and impact strength mitigate against the use of the alloy for aerodynamic turbine parts.

Finally, studies were conducted to establish the effect of material processing on the stability of Stellite 6B; and to determine whether there were any procedures available whereby the material might be rendered stable against the elevated temperature reaction. Alloy chemistry control and an extreme rapid cool, produced by salt bath quenching after solution annealing, appear to be two promising methods of preventing the elevated temperature reaction, at least up to 1065°F.

I. INTRODUCTION

SNAP-8 is a 35 kw nuclear-electric power conversion system for use in space environment. The system operates on a mercury Rankine cycle using NaK (eutectic sodium-potassium mixture) as heat-input and heat-rejection working fluids. The power conversion system is being developed by Aerojet-General Corporation for the National Aeronautics and Space Administration. The nuclear reactor is being developed for the Atomic Energy Commission by Atomics International.

The power conversion system (Figure 1) uses mercury as a working fluid and is coupled to the reactor cooling loop by a heat exchanger (boiler) where the mercury is preheated, vaporized, and superheated. The superheated vapor drives a turbine-alternator assembly which develops the 400 Hz electrical output of the system. The saturated mercury vapor leaving the turbine passes through a condenser and then to a mercury pump to complete its cycle. Cooling for the condenser is provided by another pump-driven NaK loop which couples the condenser and space radiator. Lubrication and cooling of the system is provided by a loop using an organic working fluid (polyphenyl ether). Lubrication is provided for the bearings in the turbine-alternator assembly and the mercury pump-motor assembly. Cooling is provided for the alternator, pumps, and electrical controls. The organic loop fluid is pump driven and has its own heat-rejection radiator.

Stellite 6B (Cobalt Base Alloy containing 30% Cr; 4.5% W; 1.15% C) was originally selected as the reference SNAP-8 turbine aerodynamic material primarily because of its excellent mercury erosion resistance established by several studies. One study, conducted by Aerojet's Electronics Division, exposed pin specimens at 700°F to impingement by 85% quality mercury vapor flowing at 1000 fps. NASA Lewis Research Center conducted another and subjected specimens to an ultrasonically induced cavitation erosion environment in 300°F liquid mercury (Reference 1). This erosion resistance, along with the material's satisfactory (compared to SNAP-8 requirements) elevated temperature properties, based on vendor's literature, and acceptable corrosion resistance in superheated vapor made Stellite 6B at that time appear as the preferred material for aerodynamic components in the SNAP-8 mercury turbine.

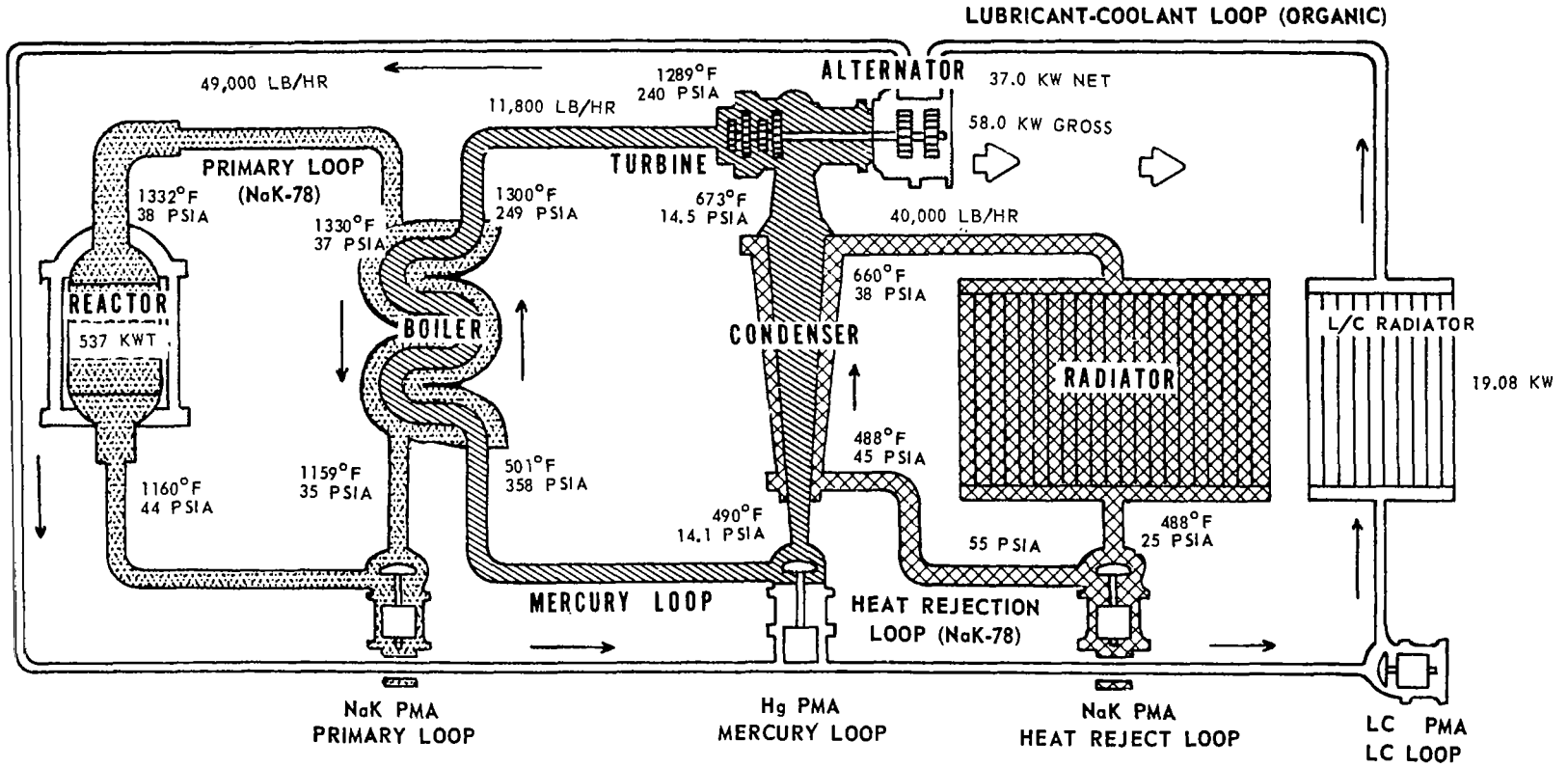


Figure 1. SNAP-8 System Schematic

SNAP-8 mercury turbines accumulated over 1000 hours operation with Stellite 6B aerodynamic parts exposed at 700° to 1250°F to mercury vapor of varying quality from approximately 75% quality to superheated vapor. Three SNAP-8 turbine failures were attributed to Stellite 6B material inadequacies. The first turbine, Assembly 3/2 S/N A-3, contained Stellite 6B components which had been given a conventional solution anneal of 2250°F, for 1 hour minimum, followed by rapid air cooling prior to machining. The parts were stress relieved at 1650°F to effect dimensional stability following rough machining. Analysis of the failed components from this turbine for the first time revealed that Stellite 6B was not metallurgically stable within the turbine operating temperature range 700° to 1250°F. This reaction was not anticipated and, in fact, not known for this material by the producer of the alloy. Preliminary testing of specimens established that a reduction in ductility and impact strength due to a metallurgical hardening reaction and volumetric contraction associated with crystallographic transformation occurred.

It was postulated that the contraction superimposed a stress in addition to the normal service stresses, the total being sufficiently high to act as a major contributor to the failure. Components for two more turbines were in fabrication at the time. Laboratory studies with samples of the heat used for component fabrication established the following thermal treatment for producing the FCC to HCP transformation:

- Step 1. Solution anneal at 2250°F, 1 hour minimum, rapid air cool
- Step 2. 1650°F, 4 hours, still air cool
- Step 3. 1250°F, 48 hours, still air cool

The resultant lower ductility was considered acceptable if dimensional changes during turbine operation did not occur. Therefore, the Stellite 6B components were transformed and hardened prior to assembly of these two turbines. When failure of Stellite 6B components during subsequent testing of these turbines occurred (shattered wheels, including corncobbing, a turbine wheel failure mode whereby many blades are separated from the hub at the blade root), it was concluded that Stellite 6B with the HCP crystallographic structure and minimum ductility was not suitable as a turbine aerodynamic material. If the accept-

ably ductile solution annealed, FCC structure could be retained during exposure to the turbine operating temperatures, Stellite 6B would be an excellent alloy candidate for mercury, and other liquid metal vapor driven, turbine aerodynamic parts where severe erosion conditions exist. A study was initiated as a result of the failure with the following objectives:

To gain an understanding of the metallurgical phenomenology involved in Stellite 6B instability at elevated temperatures.

To evaluate the effects of the metallurgical changes caused by the instability on the properties of Stellite 6B, and to establish how they may affect potential use of the material.

To perform a preliminary evaluation of potential methods for stabilizing the material against the elevated temperature reaction.

II. METALLURGICAL EFFECTS CAUSED BY ELEVATED TEMPERATURE EXPOSURE

A. PRECIPITATED CARBIDES

Stellite 6B was used in the conventional solution annealed condition which required holding at 2250°F for one hour minimum followed by rapid air cooling. In this condition the material consisted of a solid solution face centered cubic (FCC) matrix containing M_7C_3 ("M" represents one, or several metallic elements combined with the carbon to form a carbide) carbide islands. This FCC matrix structure was the equilibrium structure within the range of 2250° down to at least 1650°F. The current work did not establish whether any reactions occurred between 1650° and 1550°F, however, below 1550°F conventionally solution annealed Stellite 6B appears metallurgically unstable. The lower limit of the temperature range of instability was not determined. Within the temperature range of 1550° down to at least 700°F, the equilibrium matrix structure appears to be HCP and gradual transformation from FCC occurs.

Within the range of temperatures 1550° down to at least 885°F, the M_7C_3 carbides appear unstable and tend to transform to $M_{23}C_6$. Upon exposure to elevated temperature, the M_7C_3 carbide islands start transforming in situ to $M_{23}C_6$. The reaction starts at the matrix-exposed surface and $M_{23}C_6$ may appear as a peripheral halo around the central, M_7C_3 area.

B. CRYSTALLOGRAPHIC STRUCTURE OF MATRIX

X-ray diffraction shows that even in the conventional solution annealed condition the Stellite 6B metallographic structure can exist as a mixture of both FCC and HCP. The ratio of the two structures can vary significantly. For example, in one group of 12 specimens from the same heat which were similarly solution annealed, the FCC content varied from 41 to 98%. The average FCC content was 64% with a standard deviation of ± 16%. No statistical difference in mechanical properties was found within this group of specimens indicating the variation in matrix crystal structure was of little consequence in determining the mechanical properties of the material. Similarly, in thermally exposed material specimens from the same heat, a complete transformation to HCP did not necessarily occur. For example, in a group of 30 specimens

exhibiting instability after elevated temperature exposure, the remaining FCC content varied from 3 to 61%. The average remaining FCC content was 32.2% with a standard deviation of ± 19.4%. The exposed predominantly HCP specimens exhibited comparable properties regardless of the variation in HCP content similar to the results of the unexposed specimens which were predominantly FCC.

Laboratory thermal exposure of additional mill heats of the alloy revealed that not only was there a difference in transformation tendency between heats, but there also appeared to be a difference between specimens taken from different bars produced from the same mill heat.

Statistical comparison of the FCC content in the solution annealed specimens and the group of elevated temperature exposed specimens described above indicated that there was a significant difference in the FCC content of the material in the two states such that it was concluded that Stellite 6B exhibited a tendency toward transformation of the crystal structure from FCC to HCP as a result of the elevated temperature exposure.

C. HARDENING MECHANISM

Based on the binary Co-Cr phase diagram, Figure 2, it appears that the formation of Co-Cr sigma phase could occur in Stellite 6B during elevated temperature exposure. However, presuming a specimen containing a total content of 30% Cr and 1% C (the approximate nominal composition), the change in matrix composition during carbide chemical transformation would go from 19.9% Cr in the matrix with all Cr_7C_3 carbides, to 13.4% Cr in the matrix with all $Cr_{23}C_7$ carbides. Thus, the matrix composition would lie in, or come closer to, the edge of the ϵ field, Figure 2, and the formation of sigma phase would be minimal or not occur depending on the exact composition and the exposure temperature. Neither metallographic examination nor X-ray diffraction of electrolytic extracts from hardened and transformed material revealed the presence of Co-Cr sigma phase. Therefore, it is not probable that the formation of this phase contributed to hardening of the alloy.

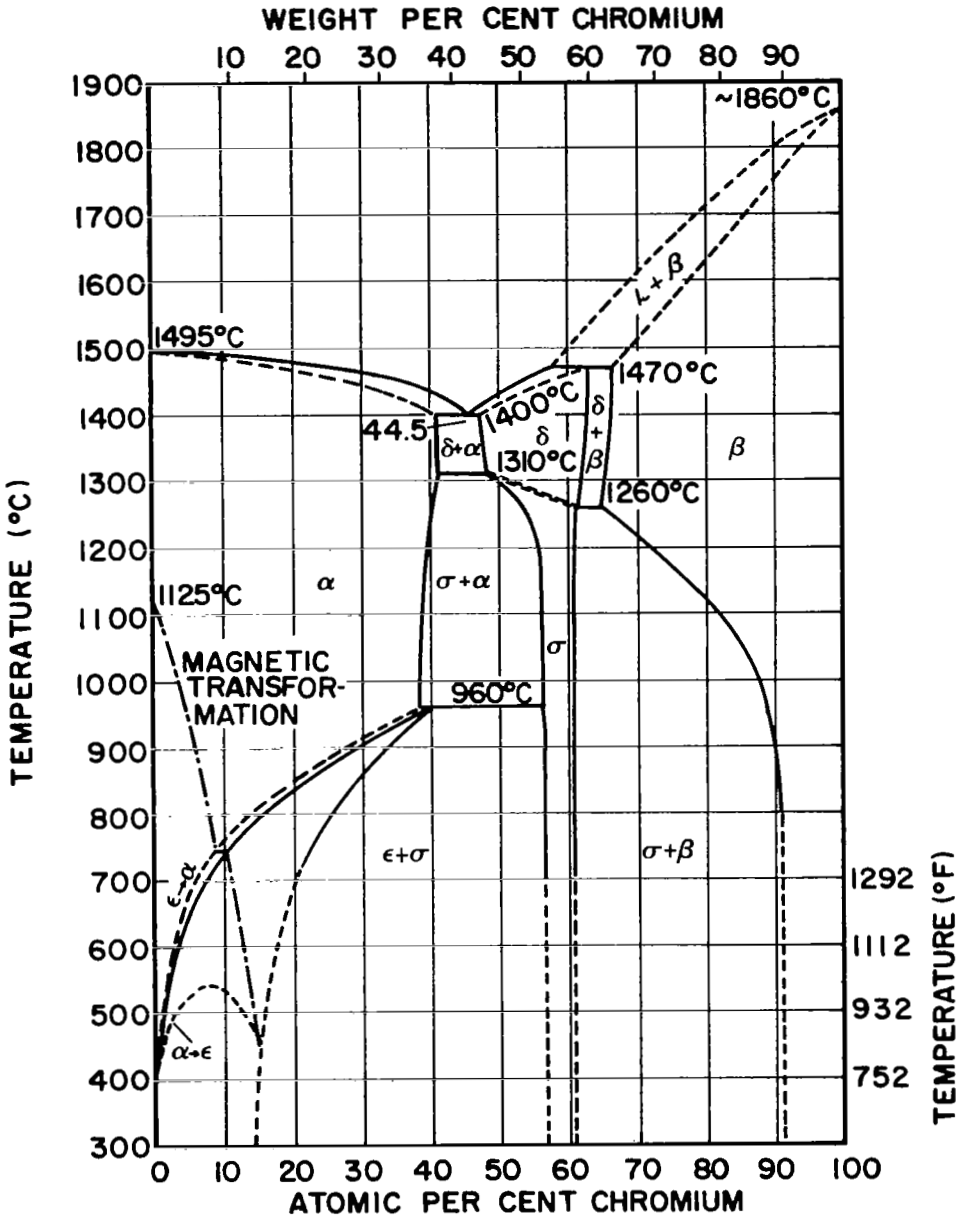


Figure 2. Cobalt-Chromium Binary Constitution Diagram

It was presumed that hardening of the matrix from Rc37-40 in the solution annealed condition to Rc48-56 after elevated temperature exposure was caused by a precipitation mechanism. It was postulated that the precipitate particles were so small that they were not visible with optical microscopy. Metallographically there was no apparent visible difference between the structures of solution annealed versus thermally exposed material other than the occasionally observed halo effect of the $M_{23}C_6$ carbide surrounding the central M_7C_3 carbide as discussed in paragraph A above. Within the matrix, the metallic composition as determined by microprobe analysis was identical whether the material was unexposed, i.e., soft and FCC, or exposed, i.e., hard and HCP. This indicated that gross metallic diffusion was not involved in the reactions. The extent of carbon diffusion was not determined. It was found, however, that a hardened HCP structure could be restored to the soft FCC structure in as little as 10 minutes exposure at 2250°F. This indicated that gross carbon diffusion was also not involved in the reaction mechanisms. However, the change in carbide form indicated that some diffusion even though over extremely short distances must have occurred.

Three matrix hardening reactions seem to have occurred during the elevated temperature exposure, within the temperature range of 885° to 1450°F, as follows:

- Minor hardening of the matrix by precipitation of another phase.
- Gross hardening of the matrix by precipitation of possibly another phase, and
- Transformation of the matrix from the FCC to the HCP structure.

It appeared that these three reactions may have occurred relatively independently in the alloy.

The hardness of the carbide islands (Rc 58-63) apparently was not altered by the hardening and transformation. Heats which responded rapidly to hardening and HCP transformation at 885° to 1450°F, underwent almost complete HCP transformation but only minor hardening (Rc 37-40 to Rc 41-42) after exposure at 700° to 850°F. Material which was 1000°F salt-bath quenched from the solution annealing temperature underwent this slight hardening when exposed

at 800° and 1065°F although the FCC matrix structure was essentially maintained. The matrix of solution annealed material which was exposed at 1650°F for four hours remained FCC structure but also exhibited a small increase in hardness and also a greater propensity toward HCP transformation and further hardening with subsequent exposure above 885°F.

The fact that both slower cooling rates from the 2250°F solution annealing temperature, and pre-exposure at 1650°F produced more rapid hardening and HCP transformation may be indicative of a nucleation and growth phenomenon contributing significantly to reactions of gross hardening and transformation of the matrix. Less time spent in the rapid carbide precipitation temperature range (1400° to 2100°F as reported by the manufacturer) results in a suppression of nucleation site formation and therefore produces greater stability of the alloy during subsequent exposure in the range of 700° to 1450°F. In this latter temperature range, although smaller, stable, nucleation sites would exist, the slower diffusion rates at the lower temperatures would limit not only their formation but their subsequent growth. Therefore, the apparent metastable low hardness and FCC structure would be retained for longer periods of time at a given elevated temperature.

III. DIMENSIONAL CHANGE ASSOCIATED WITH CRYSTALLOGRAPHIC TRANSFORMATION

The linear dimensional change of Stellite 6B due to transformation from the FCC to the HCP crystal structure was determined on 18 parts using 91 individual measurements. Linear contraction resulted from the transformation as would be predicted based on the more closely packed atomic arrangement of the HCP crystal structure compared to FCC. The average linear contraction and the standard deviation of the 91 individual measurements were 0.092% and 0.042%, respectively. Based on these data and on the assumption that a normal distribution exists, there is a 99% probability that 99% of the measured contractions due to the crystallographic transformation of Stellite 6B will fall between 0 and 0.223% (see Figure 3).

There are several probable reasons for the standard deviation ($\pm$ 0.042%) being significantly large compared to the average contraction (0.092%). Among these are: fabrication history, residual machining stress patterns, and the specimens selected at random from the bulk material.

Any dimensional changes of a part in service are considered detrimental. Potential resultant changes in tolerance buildup, clearances, and stress patterns are undesirable and represent a high probability failure mechanism.

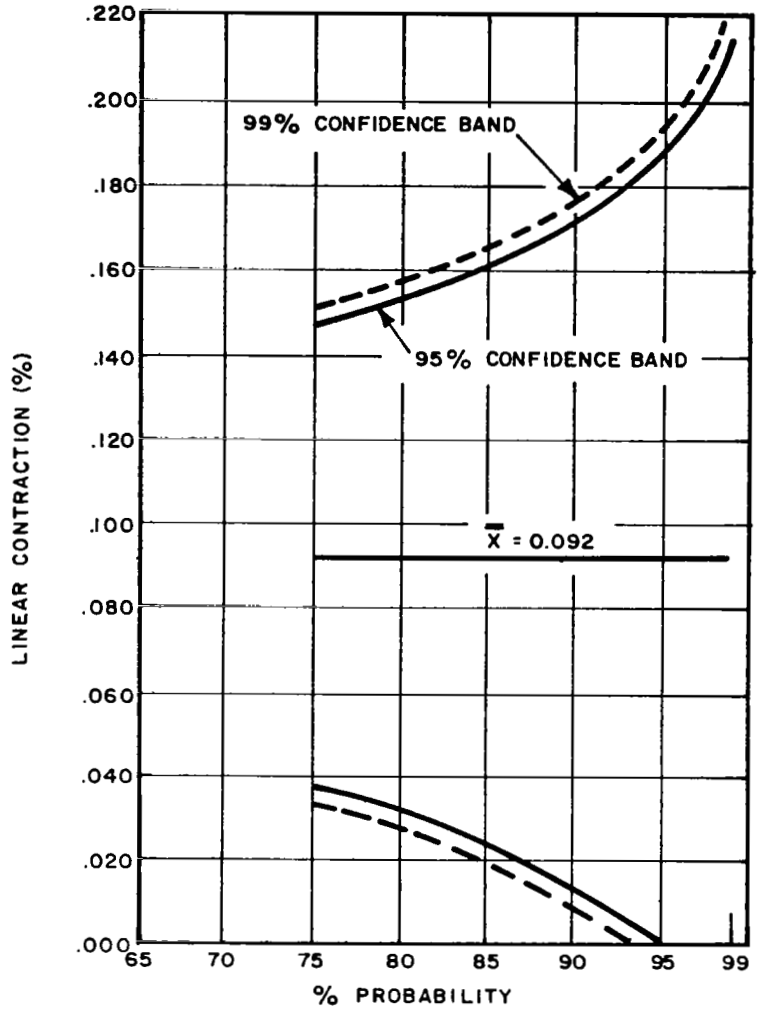


Figure 3. Statistical Linear Contraction of Stellite 6B During Crystallographic Transformation from FCC to HCP

IV. MECHANICAL PROPERTY EFFECTS

Mechanical properties of Stellite 6B were determined by tests in the temperature range of 75° to 1350°F. Cursory tests for some properties were run to establish trends which could be compared to published data. The data were sufficient to indicate the effect of the high temperature instability of the solution annealed alloy. A marked reduction in ductility and impact strength occurred with only slight, if any, changes in other properties evaluated.

A. SPECIMEN PREPARATION

Tensile tests were conducted on specimens machined from Stellite 6B bar stock, 5/8 inch diameter, before and after a thermal treatment which promoted the elevated temperature reaction. An ancillary laboratory study was conducted by thermally exposing specimens at various temperatures to determine a cycle which would produce the elevated temperature metallurgical reactions. It was presumed, based on a time/temperature relation of the elevated temperature reaction of solution annealed material, that specimens of comparable hardness (i.e., above Rc 46) would exhibit comparable properties regardless of the exposure temperature used to produce this hardness. Specimens were prepared from the same heat of material and solution annealed, soaked at 1650°F for 4 hours, then exposed at 1450°F until the metallurgical reaction produced a minimum hardness of Rc 46. A variable soaking time at 1450°F for 732 to 1550 hours was required. The metallurgical characteristics of the material before and after exposure were established by X-ray diffraction and hardness tests.

The test specimens for evaluating the dynamic modulus of elasticity, torsional modulus, and Poisson's ratio were machined from 3/4 inch thick plate stock, heat No. 1094, of the following chemistry:

C	1.04	Si	0.82
Cr	29.00	Ni	1.46
W	4.61	Mo	0.15
Mn	0.84	Fe	0.75

Co Balance

Flexure and impact tests specimens were prepared from a different single mill heat of material, heat No. 1050, of the following chemistry:

C	1.05	Si	0.94
Cr	30.84	Ni	1.32
W	4.33	Mo	0.14
Mn	0.88	Fe	0.76

Co Balance

The specimens were machined from available material which included as-received pancake forging blanks or actual parts which had operated in a SNAP-8 turbine. One consequence of using semi-processed or fully processed parts was that there was no freedom in selecting the orientation of the specimen within the part envelope. A variation in the test results would be anticipated due to the anisotropic properties of the test specimens.

B. TEST PROCEDURES

Tensile tests were performed in accordance with the procedure described in ASTM-E21-58T, using a 10,000 pound capacity Instron testing machine. The load was applied to the specimen at a rate of 0.05 inch per minute crosshead speed. The extensometer was attached to the specimen across a one inch gage length and electrically coupled to the tensile machine so that a load-strain curve was obtained on an X-Y recorder during the test.

Flexure tests were performed on rectangular specimens. A Riehle 60,000 pound Universal Testing Machine set on the 600 pound range was employed to apply the load to the specimen at a crosshead speed of 0.05 inch per minute. A Riehle Deflectometer set at a magnification ratio of 175 was positioned under the center of the specimen to detect deflection and was coupled electrically to the testing machine X-Y recorder to provide a continuous plot of deflection versus applied load. The load was applied until specimen failure occurred.

The ultimate flexural strength and the modulus of elasticity were determined from the following relationships:

$$U = \frac{3SL}{2wt^2}$$

where:
- U = ultimate flexural strength (psi)
- S = span length (inches)
- L = ultimate load (pounds)
- w = specimen width (inches)
- t = specimen thickness (inches)

and,

$$f = \frac{WS^3}{48EI}$$

where:
- f = deflection (inches)
- W = load (pounds)
- S = span length (inches)
- E = modulus of elasticity (psi)
- I = rectangular moment of inertia about the neutral axis of the specimen ($inches^4$)

Charpy impact tests were performed in accordance with the general procedure of Sections 22 to 24 of ASTM A-370-61T, using a National Forge and Ordnance Company testing machine whose hammer had twenty foot-pounds of energy and a striker velocity of 11.3 feet per second at impact.

The testing procedures for evaluating the dynamic modulus of elasticity, torsional modulus, and Poisson's ratio were performed employing an FM-500 Elastomat Unit and piezoelectric transducers. The test method involved the determination of the fundamental resonant frequencies of a cylindrical specimen at each of several test temperatures. Calculations for determining specific properties from the test data were based on the relationships described in Appendix A.

C. TEST RESULTS

The test data tabulated in Tables 1 and 2 were plotted in Figures 4 through 6. Thermally exposed Stellite 6B exhibits poor plastic deformation characteristics. Thermal stresses, occurring for example, during operation of a turbine, would not be accommodated easily by local deformation. As the test temperature is increased above 1000°F, an improvement in ductility of the thermally exposed specimens occurs, as shown in Figure 5, but the ductility level is extremely low when compared with that of the unexposed specimens. The comparative brittleness of the exposed specimens persists at temperatures up to 1250°F.

Material in the thermally exposed condition exhibited lower ultimate flexural strength (15% reduction) and lower ductility, i.e., deflection (66% reduction) than material in the unexposed condition (see Table 3). The tests indicate the thermally exposed turbine wheel specimens possess a lower ductility (i.e., deflection and ultimate flexural strength) than the unexposed specimens.

The impact test results shown in Table 4 indicate that hardened material in the HCP condition has a 70% lower impact strength than material in the softer FCC condition.

An increase in Poisson's ratio and a decrease in torsional and elastic moduli with increasing test temperature was measured. The dynamic modulus of elasticity was considerably higher and indicated less temperature sensitivity than that reported in the literature, see Figure 7. The reason for the variation between the moduli determined by the two different methods is not clear. A difference may be due to strain rate sensitivity and nonconformance to Hook's Law for this material at the high frequencies (3000 to 20,000 Hz) and low stress levels employed in these tests.

TABLE 1

SHORT TIME TENSILE PROPERTIES OF UNEXPOSED, SOLUTION ANNEALED[1] STELLITE 6B

Specimen No.	Hardness (R_C)	Structure[2] (% FCC)	Test Temp. (°F)	0.2% Yield Strength (psi x 10^3)	Ultimate Strength (psi x 10^3)	Elongation (% in 1 in.)	Reduction of Area (%)
1	41.5	46	Room	90.6	152.0	9.0	7.1
2	41.5	63	Room	86.5	152.8	10.0	6.9
3	41.5	57	Room	93.1	155.7	10.0	9.1
4	41.5	55	400	74.2	145.7	12.0	11.8
5	41.5	78	400	73.9	151.3	15.0	13.3
6	41.5	65	400	73.0	147.6	14.0	13.6
7	41.0	60	800	62.8	147.9	17.5	16.7
8	41.5	71	800	65.5	147.4	16.0	15.9
9	41.5	81	800	61.6	147.1	18.0	17.3
10	40.5	98	1200	62.0	125.9	13.5	11.7
11	39.5	41	1200	61.5	124.8	15.0	12.3
12	40.0	53	1200	62.1	124.2	13.0	12.2

(1) 2250°F - 2 Hrs. - Rapid Air Cool.

(2) Estimated by X-ray diffraction analysis. Accuracy ± 10%.

TABLE 2

SHORT TIME TENSILE PROPERTIES OF ELEVATED TEMPERATURE EXPOSED[1] STELLITE 6B

Specimen No.	Hardness[2] (Rc)	Structure[3] (% HCP)	Test Temp. (°F)	0.2% Yield Strength (PSI x 10^3)	Ultimate Strength (PSI x 10^3)	Elongation (% in 1 in.)	Reduction of Area (%)
1	46	92	Room	103.9	153.5	2.4	1.8
2	46	89	Room	115.9	155.0	2.3	1.4
3	47	90	Room	98.4	148.0	2.1	1.4
4	47	92	Room	104.7	156.1	2.4	1.4
5	48	92	Room	100.8	163.6	3.0	2.2
6	48	93	Room	104.0	168.1	2.0	2.0
7	48	70	400	107.9	144.7	2.9	2.4
8	48	84	400	96.2	143.3	3.0	3.0
9	47	77	400	104.2	143.5	3.2	2.2
10	47	52	700	85.4	138.9	3.3	4.2
11	46	59	700	102.2	137.6	3.0	2.6
12	48	56	700	97.2	143.3	3.0	2.6
13	48	92	800	92.4	141.4	2.8	3.4
14	48	50	800	102.0	144.6	3.3	3.0
15	48	61	800	97.2	144.2	3.4	3.4
16	48	64	900	95.2	143.6	3.0	2.3
17	48.5	47	900	93.6	142.8	3.2	3.0
18	48	60	900	94.3	143.5	3.3	3.4
19	48	51	1000	95.4	145.1	2.8	3.0
20	48	53	1000	88.6	140.3	3.2	3.2
21	48	77	1000	97.0	147.9	2.5	2.4
22	48	50	1100	89.6	136.4	3.0	3.0
23	48	65	1100	89.6	137.4	3.4	3.8
24	48.5	49	1100	94.8	142.9	3.1	3.6
25	48	43	1200	89.3	133.4	3.5	4.8
26	48	44	1200	95.7	135.4	3.3	4.5
27	48	39	1200	91.5	140.6	3.7	4.0
28	48	97	1250	92.7	134.2	3.8	3.8
29	48.5	96	1250	90.7	136.7	3.5	4.6
30	48	50	1250	88.3	131.4	3.5	4.4

(1) Solution Annealed Material at 2250°F - 2 hrs - Rapid Air Cool. Subsequently conditioned at 1650°F for 4 hrs., then exposed at 1450°F until Rc 46 minimum hardness measured. Exposure time varied up to 1550 hrs.

(2) At room temperature (75°F).

(3) Estimated by X-ray diffraction analysis. Accuracy ± 10%.

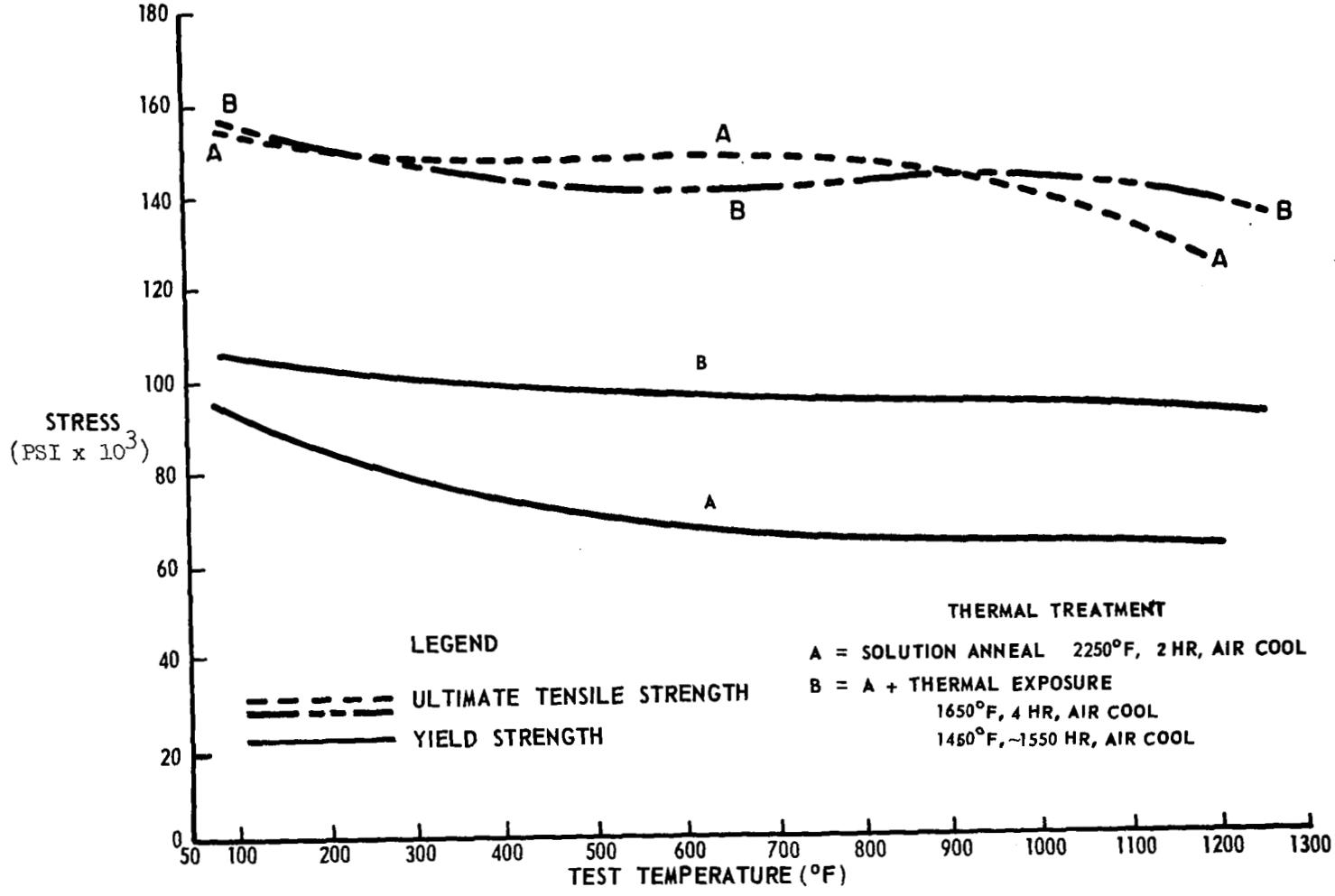


Figure 4. Short Time Ultimate and Yield Strengths of Solution Annealed and Thermally Exposed Stellite 6B

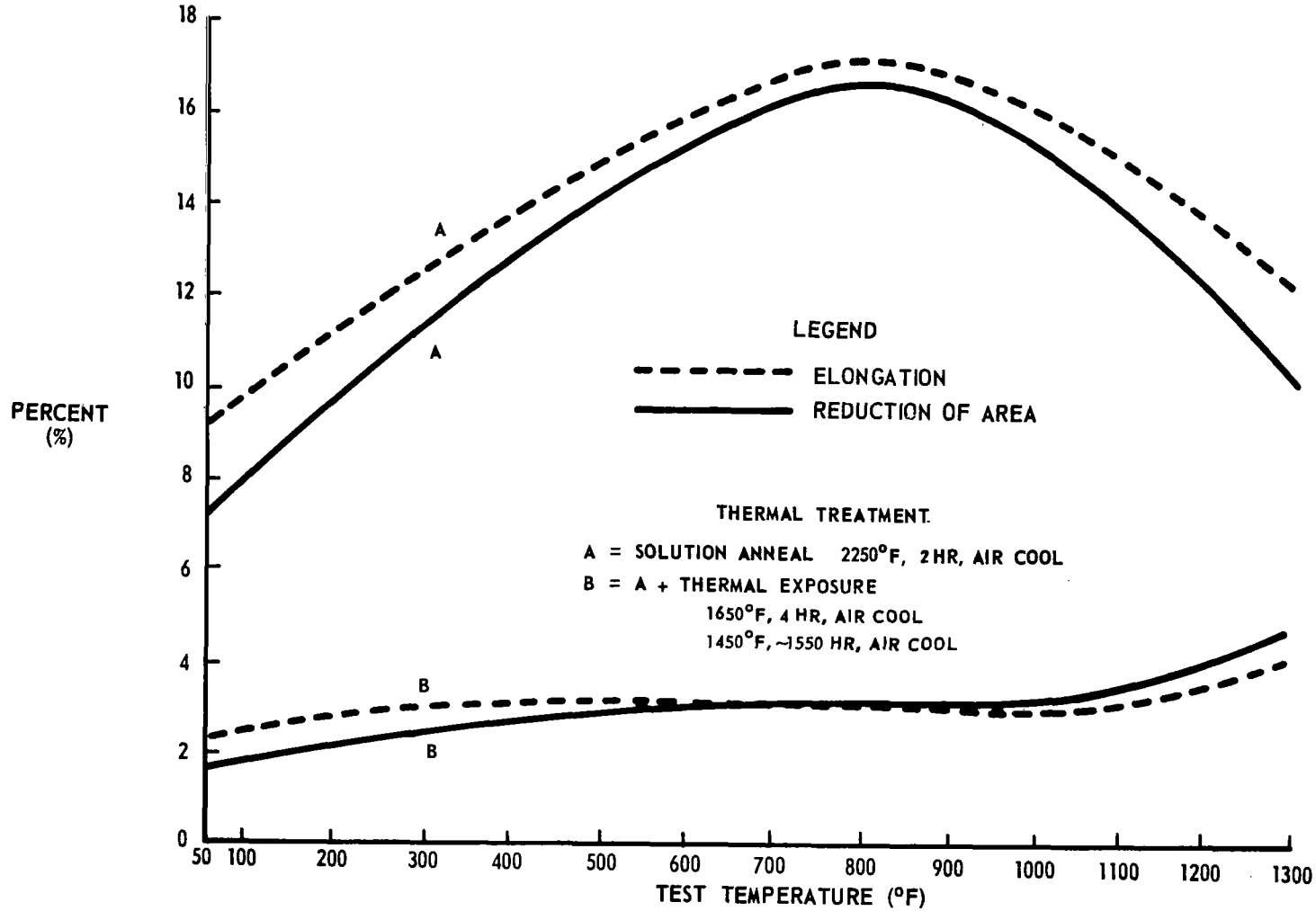


Figure 5. Short Time Elongation and Reduction of Area of Solution Annealed and Thermally Exposed Stellite 6B

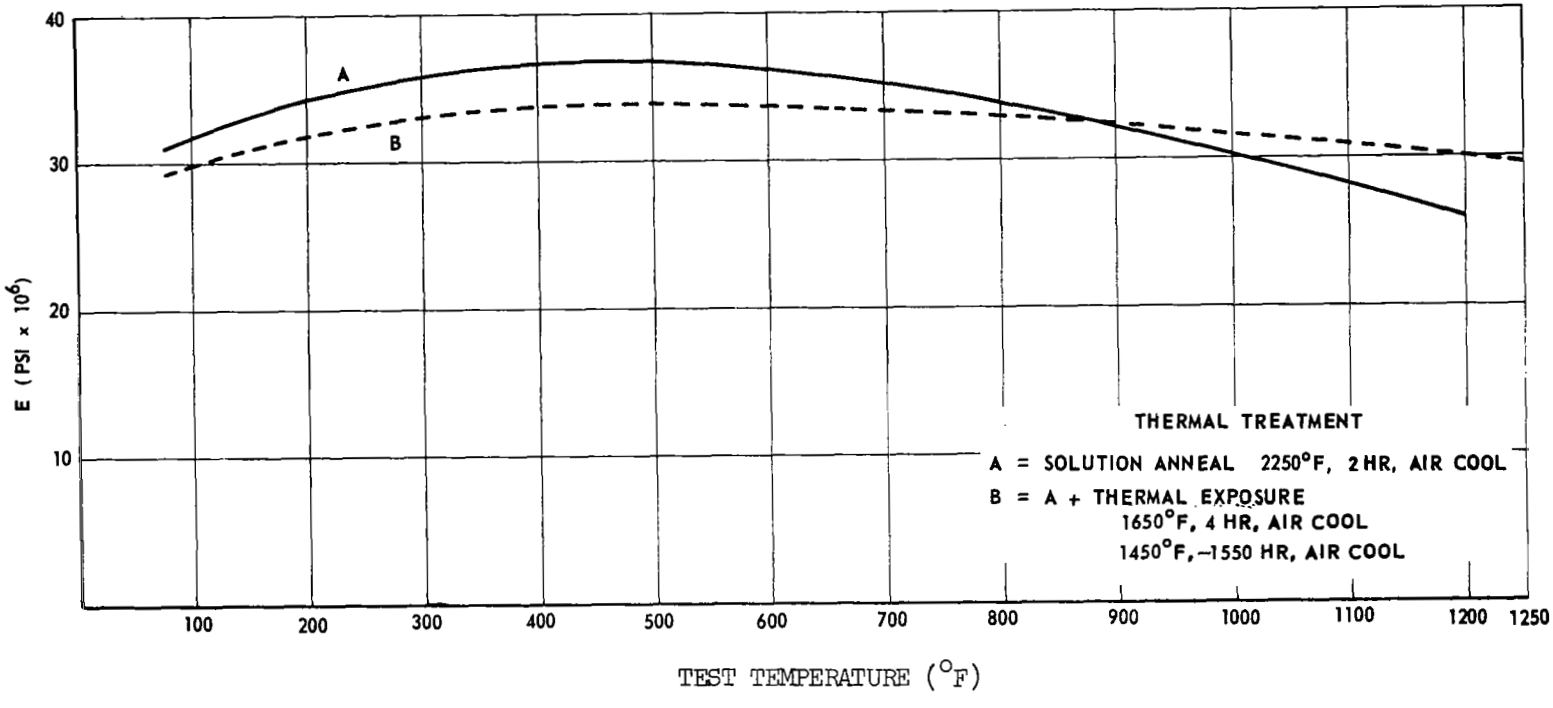


Figure 6. Modulus of Elasticity of Solution Annealed and Thermally Exposed Stellite 6B

TABLE 3

STELLITE 6B FLEXURE TEST RESULTS

Test No.	Specimen[1]	Condition	Structure[2]	Ultimate Flexural Strength[3] ($psi \times 10^3$)	Deflection at Failure[3] (mils)	Hardness[3] (R_c)	Modulus of Elasticity[3] ($psi \times 10^6$)
1.	Forged blank	Unexposed	FCC	242 (236-248)	100 (112-88)	40 (40-40)	30
2.	Forged blank	Furnace exposed at 1200°F for 90.5 hr	HCP	206 (200-211)	34 (32-35)	49 (49-49)	42 (44-40)
3.	SNAP-8 Turbine 2nd stage wheel	Exposed at 897-937°F for 819 hr during Turbine Operation	HCP	235	39	51	33
4.	SNAP-8 Turbine 3rd stage wheel	Exposed at 801-819°F for 819 hr during Turbine Operation	Primarily HCP with some FCC	229	70	42	35
5.	SNAP-8 Turbine 4th stage wheel	Exposed at 703-704°F for 819 hr during Turbine Operation	Primarily HCP with some FCC	186	43	41	33

(1) Three Point Loaded Specimen. Cross-section 0.395 in. wide x 0.110 in. thick. Test span 2 in. These specimens were solution annealed at 2250°F for 2 hr, rapid air cooled and then stress relieved at 1650°F for 4 hr.

(2) Estimated by X-ray diffraction before test. FCC-Face Centered Cubic Structure: HCP-Hexagonal Close Packed Structure.

(3) Individual test values appear in parenthesis where two tests were run.

(4) These specimens were solution annealed.

TABLE 4

STELLITE 6B CHARPY UNNOTCHED IMPACT TEST RESULTS

Test No.	Specimen[1]	Predominant Crystal Structure[2]	Hardness[3] (Rc)	Impact Strength[3] (Foot-Pounds)
1	Unexposed specimen	FCC	40 (40-40)	4.2 (5.0-3.5)
2	Furnace exposed at 1200°F for 90.5 hours	HCP	49 (49-49)	1.2 (1.3-1.1)

(1) All specimens fabricated from a turbine wheel forging blank which had been annealed at 2250°F for 2 hours, rapid air cooled, then stress relieved at 1650°F for 4 hours.

(2) Estimated by X-ray diffraction analysis
FCC - Face Centered Cubic
HCP - Hexagonal Close Packed

(3) Values in parentheses represent range of results. Single value represents average of results.

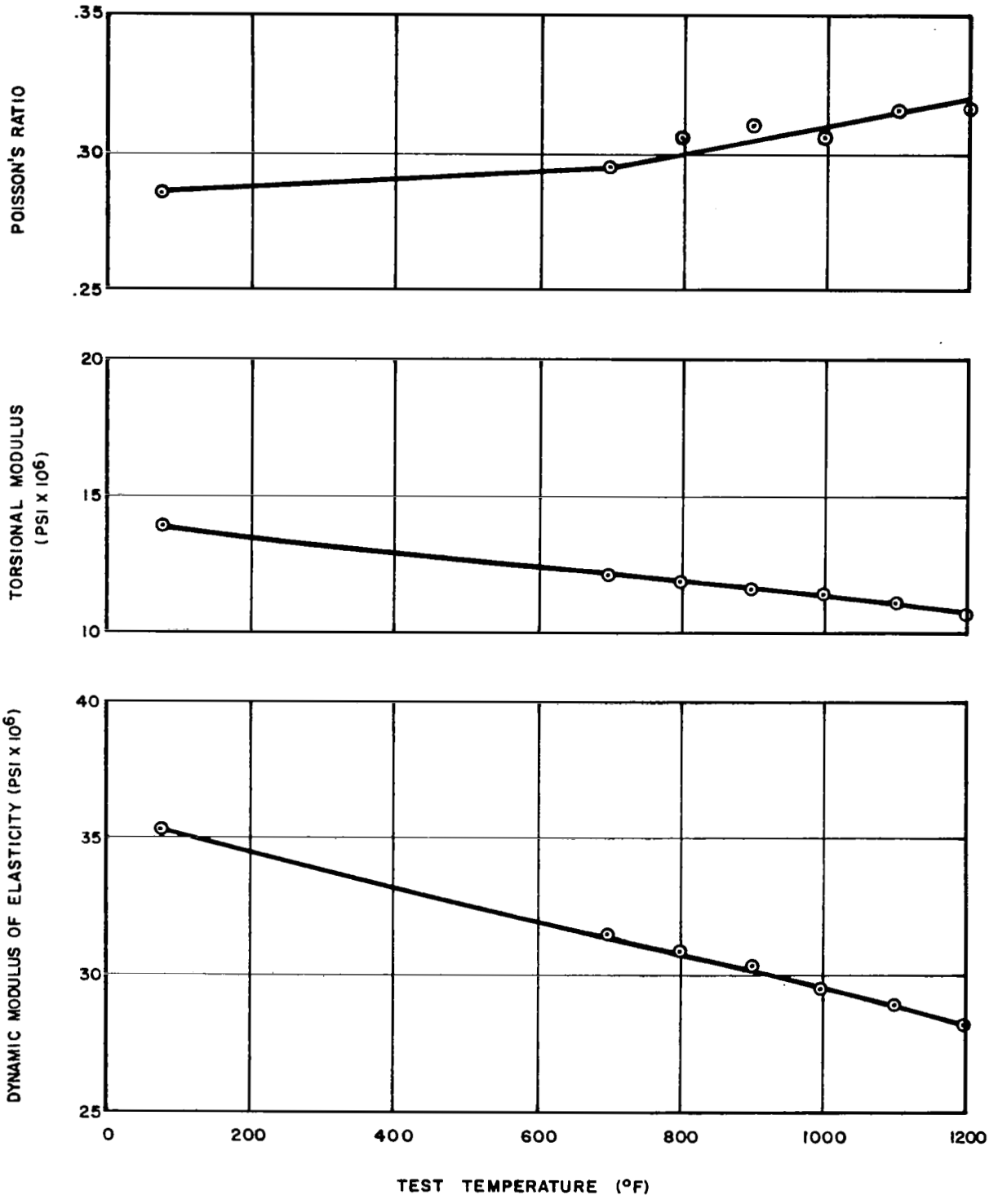


Figure 7. Properties of Thermally Exposed Stellite 6B

D. DISCUSSION

The ultimate strengths of the thermally exposed and the solution annealed Stellite 6B appear to be comparable as shown in Figure 4. The thermally exposed Stellite 6B exhibited a moderately higher tensile yield strength and the tendency for brittle failure as evidenced by 75% loss in elongation and reduction of area which indicates the incapacity for local plastic deformation. This incapacity was further indicated by the significant reduction in ductility (i.e., deflection) during the flexure test. As a consequence, special care must be exercised in designing parts and assemblies to minimize stress raising notches since the material cannot relieve these high local stresses except by fracturing. This lack of deformation capability was apparent in the evaluated components of the SNAP-8 turbine which failed after 819 hours of operation. It was estimated that those parts of the turbine exposed to the higher temperatures operated in excess of 500 hours after transformation had taken place. Some of the parts apparently had relieved localized stresses by cracking during operation prior to the catastrophic failure.

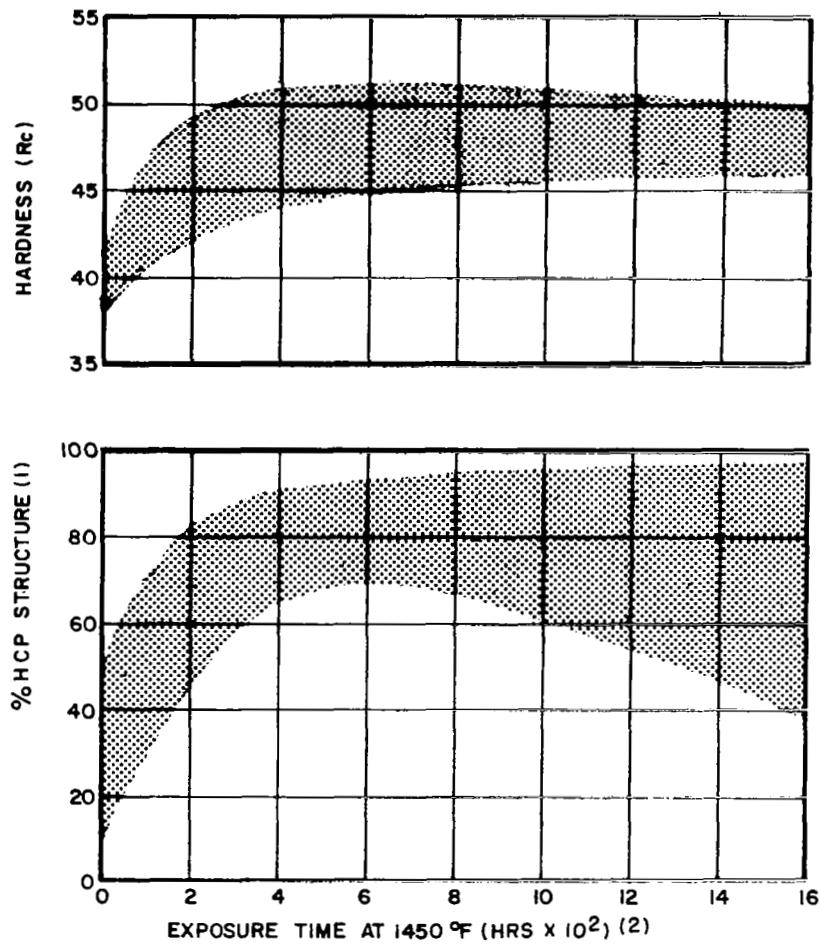
V. STABILIZATION STUDIES

A. EFFECT OF MATERIAL PROCESSING

It has been observed that not only different heats of material but also specimens from different locations in the same piece of material harden and transform at considerably different rates. Laboratory tests on samples from various heats of conventionally solution annealed material exhibiting a propensity for hardening and transformation indicated that a thermal treatment of holding at 1650°F for 4 hours plus 1250°F for 48 hours caused essentially complete transformation to the HCP condition and hardening to Rc 48 to 51. Subsequently, 36 production parts fabricated from these heats were heat treated in the same manner. All of the parts transformed to a predominantly HCP condition and 33 of them had hardnesses of Rc 48 to 51. However, one part had a uniform hardness of Rc 44 and two parts had a hardness of Rc 49 with localized areas of Rc 46.

Heat No. 1036 not only showed a general sluggishness to transformation and hardening but also a variation in response to thermal exposure between different locations in the same 5/8 inch diameter bar. Initial exposures at temperatures between 1250° and 1550°F indicated that although sluggish, the most rapid hardening and transformation occurred at 1450°F for this heat of material. The material was, therefore, held at 1650°F for four hours followed by exposure at 1450°F for varying times up to 1550 hours. The variation in transformation and room temperature hardness (specimens were periodically cooled to room temperature for hardness measurements) as a function of exposure time at 1450°F are shown in Figure 8.

The data indicate that presently unknown variables influence the mechanism of transformation and hardening. Determination of the cause of the variations observed may permit the incorporation of those conditions in material processing which will provide the greatest metallurgical stability of Stellite 6B at elevated temperature.



(1) ESTIMATED BY X-RAY DIFFRACTION ANALYSIS. ACCURACY ± 10%.
(2) PRIOR TO EXPOSURE, PARTS WERE SOLUTION ANNEALED AT 2250°F 1 HR, AIR COOLED, THEN HELD AT 1650°F 4 HRS, AIR COOLED

Figure 8. Effect of Elevated Temperature Exposure on Different Stellite 6B Specimens from Heat No. 1036

B. STABILIZATION BY HEAT TREATMENT

Variations in the heat treatment of Stellite 6B resulted in changes in the rate of transformation and hardening of the alloy during subsequent thermal exposure. The standard solution annealing treatment for this alloy was to hold at 2250°F for one hour, minimum, followed by a rapid air cool. As part of SNAP-8 turbine fabrication, most of the Stellite 6B components were further heat treated at 1650°F for four hours after rough machining to minimize the effects of residual stresses on distortion during turbine operation. After 819 hours of operation between 700° and 1240°F, the parts which had been thermally treated in this manner had transformed essentially completely to the HCP structure. However, one part in the assembly was stress relieved at 1100°F rather than 1650°F and after the 819 hours of operation at a temperature of 1160°F this part had essentially retained the FCC structure. The only known difference in fabrication of this part was the lower stress relieving temperature employed. This indicated the possibility that a precipitation-phenomenon occurring at temperatures above 1160°F may contribute to the rate of transformation during subsequent exposure. If this assumption is correct, then not only exposure above 1160°F for a finite period, but also the dwell time above this temperature during the cooling procedure (i.e., cooling rate) inherent in solution annealing may have an effect.

To determine the effect of the cooling rate from the solution annealing temperature of 2250°F on the rate of transformation, two full size forgings and a small section of a forging from one mill heat No. 1051 were annealed at 2250°F and air cooled. Subsequently, one of the two full size forgings was stress relieved at 1650°F for 4 hours.

These three specimens represented combinations of two variables:

- Cooling rate - fast rate (small forging) vs slow rate (large forgings)
- Thermal history - solution annealed vs solution annealed and stress relieved (the variation applied to the two large forgings)

If precipitation during cooling influenced subsequent transformation, the full size forgings would be expected to exhibit the greatest effect. Further, if a stress relief above 1160°F during fabrication resulted in precipitation, which enhanced transformation during subsequent extended temperature exposure, it was anticipated that the forging which was stress relieved at 1650°F for 4 hours after a solution annealed at 2250°F would transform most rapidly.

A section of each of the three heat treated parts was thermally exposed in an air furnace at 1200°F. The change in structure was estimated periodically by removing the specimen from the furnace and performing an X-ray diffraction analysis at room temperature. There is no effect on the prevailing crystal structure of the specimen produced by this periodic thermal cycle to room temperature if the exposure temperature remains below 1550°F as discussed in Section II, A above. The effect of the exposure is illustrated in Figure 9.

These results do in fact indicate that the cooling rate from 2250°F does affect the transformation rate. The most rapidly cooled specimen retained approximately 43% FCC structure after 1110 hours of exposure and the more slowly cooled specimen transformed to the HCP structure within 450 hours of exposure at 1200°F. The results also indicated that the 1650°F stress relieving treatment also increased the rate of transformation; the specimen representing the slowest cooling rate from the annealing temperature and with the 1650°F stress relief treatment had essentially transformed completely to the HCP structure within 96 hours at 1200°F.

To determine if a cooling rate more rapid than air cooling from the annealing temperature would further increase the sluggishness to transformation, sections of Stellite 6B were annealed at 2250°F and quenched in salt at 1000°F. This treatment provided a faster cooling rate than air cooling and would also be practical for use with production parts. Sections of the salt quenched material were subsequently exposed at 800° and 1065°F. In the first 400 hours of exposure, the hardness of both specimens increased to Rc 40 from the annealed hardness of Rc 37. No further change in structure or hardness occurred in 4603 hours at 1065°F or in 1025 hours at 800°F (see Figures 10 and 11). The specimen exposed at 800°F was subsequently exposed

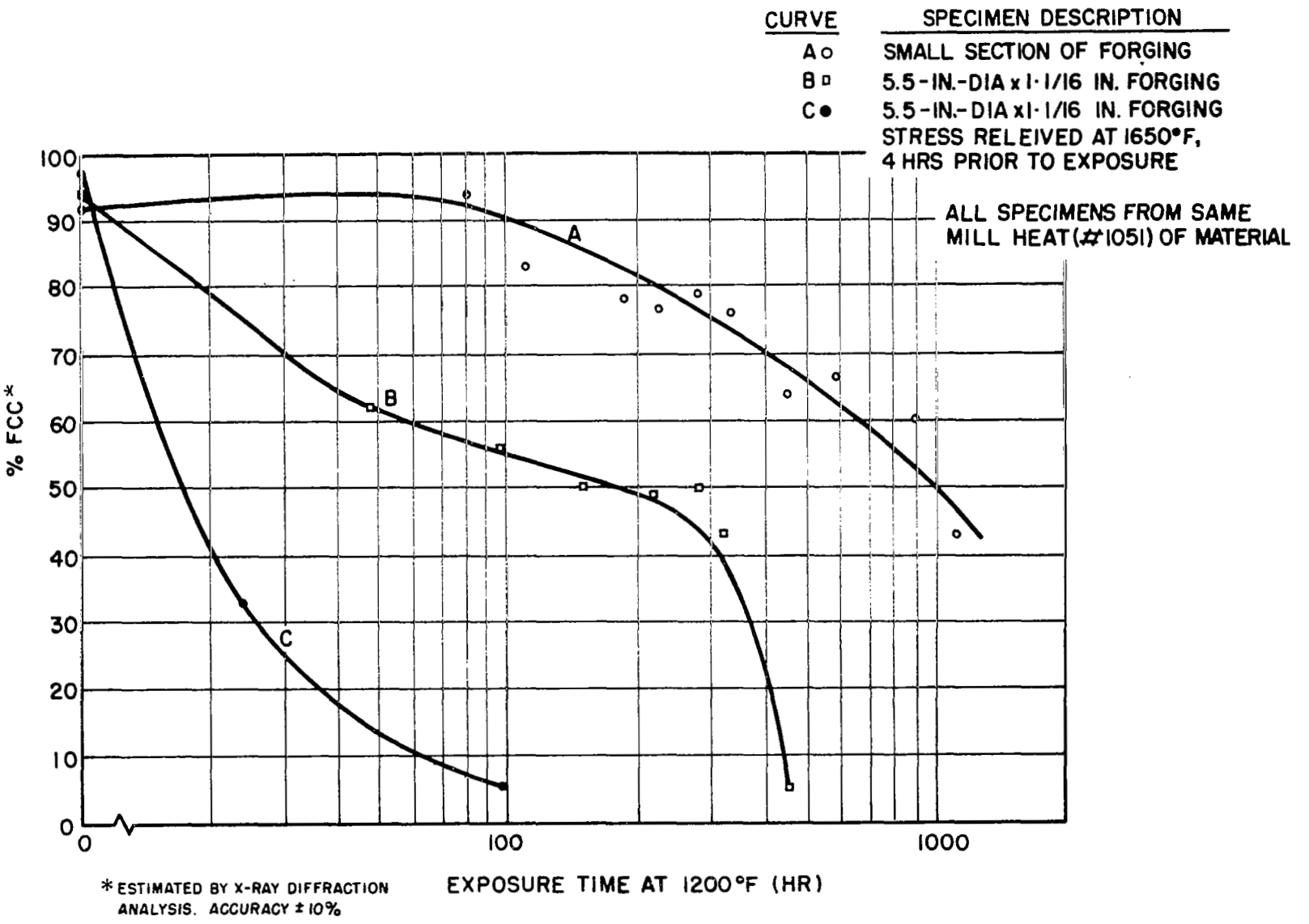


Figure 9. Effect of Air-Cooling Rate from the Solution Annealing Temperature (2250°F) on Stellite 6B Transformation from FCC to HCP at 1200°F

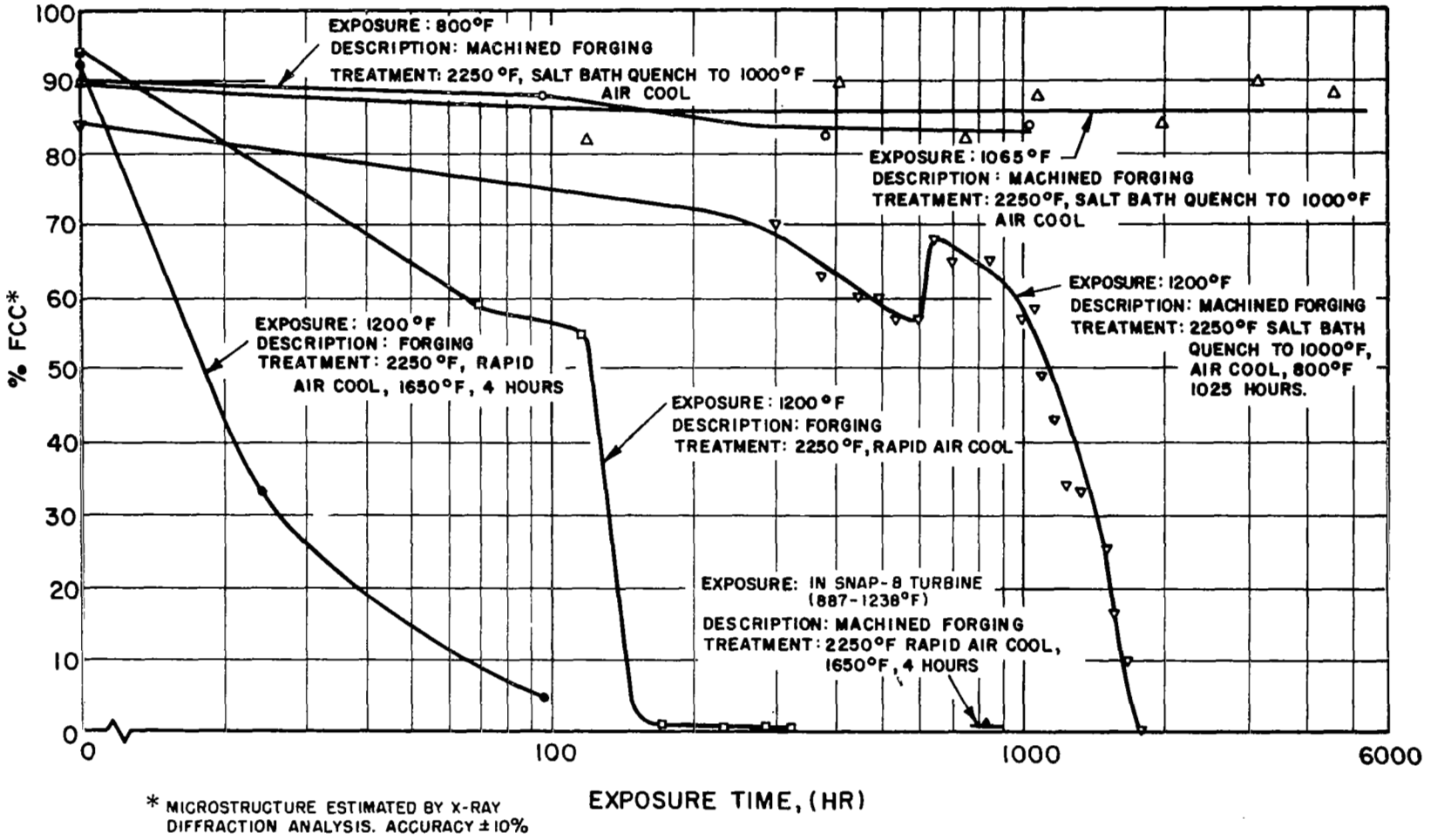


Figure 10. Effect of Heat Treat Procedure on the Transformation of Stellite 6B at Elevated Temperature

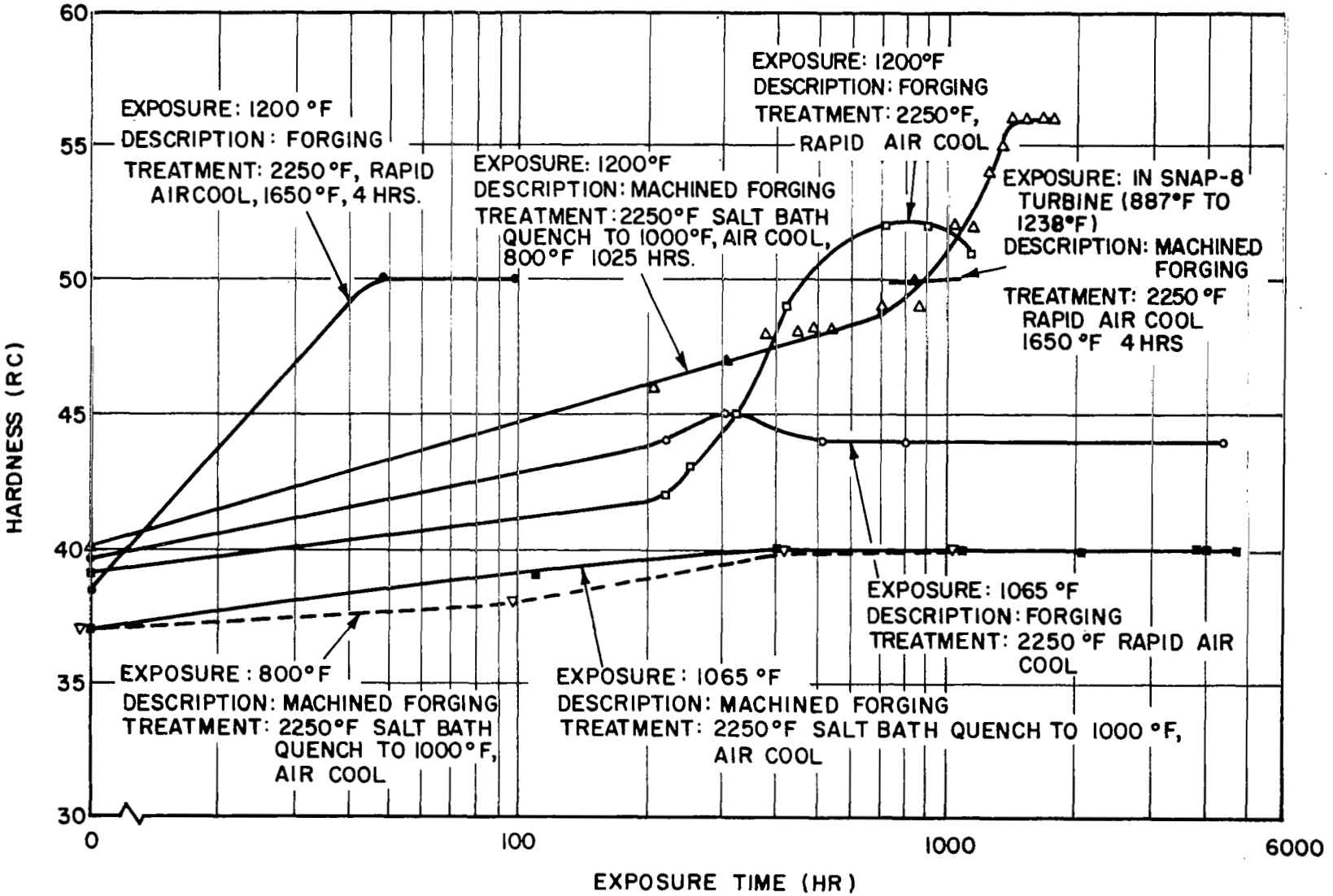


Figure 11. Effect of Heat Treat Procedure on the Hardening Characteristics of Stellite 6B at Elevated Temperature

at 1200°F. After 1750 hours exposure at 1200°F the structure had transformed to essentially all HCP and the hardness had increased to Rc 56 (see Figure 10).

In summary, the rate of transformation from FCC to HCP and the rate of hardening of Stellite 6B can be significantly influenced by prior thermal history. A very rapid cooling from the solution annealing temperature by salt bath quenching produces a structure which appears stabilized against the elevated temperature reaction up to at least 1065°F.

C. STABILIZATION BY CHEMISTRY CONTROL

Samples of ten different commercial heats of solution annealed Stellite 6B were heat treated by holding at 1650°F for four hours followed by holding at 1250°F for 48 hours. After the heat treatment, a diffractometer X-ray diffraction trace was made of each sample. The samples were then qualitatively classified as to exhibited tendency to react to the elevated temperature exposure (see Table 5). Based on the previous observation that the tendency of the metal to transform from FCC to HCP was associated with the elevated temperature instability, this criteria was used to determine stability or the lack of it.

Distinct differences in the tendency to transform were noted between groups of specific heats; each was either less than 15% or greater than 80% HCP after exposure. The chemical composition and the effect of the thermal treatment on the transformation of each sample are listed in Table 5. Since the exact mechanism of transformation and hardening in this alloy was not known, and since chemical composition is known to influence transformations, Reference 6, a comparison between the chemical composition and the tendency to undergo transformation to the HCP structure was made. Figure 12 is a plot of the arithmetic sum of the FCC stabilizing elements versus the sum of the HCP forming elements, with no weighing as to relative effectiveness, for each heat. Two fairly distinct groupings are apparent. Within the permissible variation in chemical analysis for Stellite 6B those heats with higher FCC forming elements and lower HCP forming elements showed less tendency for transformation to the HCP structure.

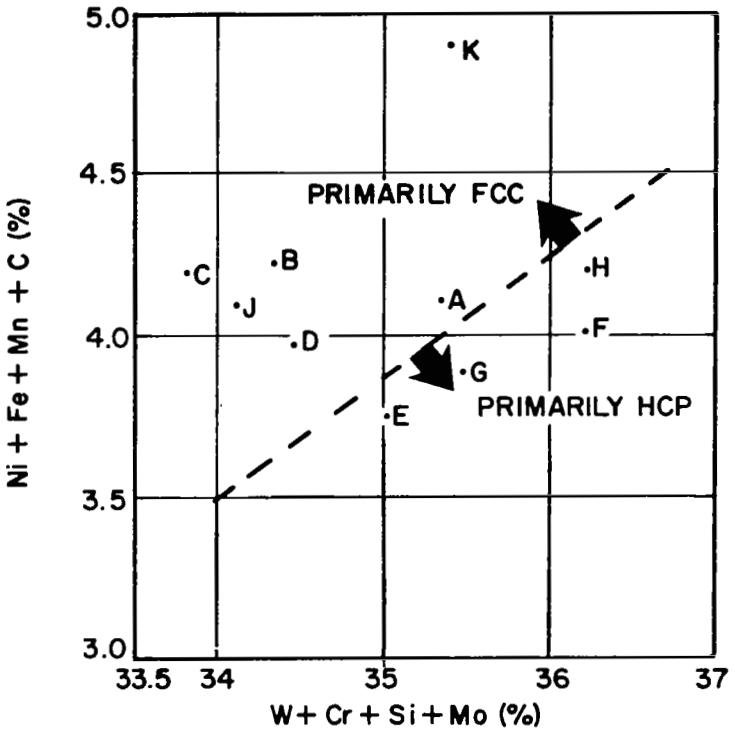
TABLE 5

CHEMICAL COMPOSITION AND TRANSFORMATION TENDENCY OF TEN HEATS OF STELLITE 6B

Heat No.(1)	Chemical Composition (weight percent)									Transformation Tendency(2)
	Cr	W	C	Fe	Si	Co	Ni	Mn	Mo	
1036(J)	29.5	4.34	1.04	1.16	.17	Bal.	1.20	.69	.10	No
1042(H)	30.7	4.44	1.08	.73	.90	Bal.	1.63	.76	.18	Yes
1050(F)	30.8	4.33	1.05	.76	.94	Bal.	1.32	.88	.14	Yes
1061(A)	29.8	5.25	1.03	1.00	.20	60.3	1.12	.96	.09	No
1063(B)	29.8	4.36	1.07	1.01	.06	61.0	1.36	.78	.11	No
1064(C)	29.2	4.27	1.18	1.09	.26	61.7	1.12	.80	.10	No
1066(D)	29.6	4.59	1.08	.99	.20	61.3	1.09	.80	.08	No
1075(G)	30.1	4.59	1.10	.79	.67	Bal.	1.28	.72	.13	Yes
1086(K)	30.0	4.51	1.06	.80	.69	Bal.	1.79	1.24	.19	No
1098(E)	30.2	4.04	1.10	.70	.66	Bal.	1.30	.65	.13	Yes

(1) Letter in parenthesis identifies heats in Figures 12 and 13.

(2) Predominate crystal structure estimated by X-ray diffraction after a solution anneal at 2250°F for 2 hrs followed by exposure of 4 hours at 1650°F plus 48 hours at 1250°F. Heats which did not tend to transform from the face centered cubic structure to the hexagonal close packed are considered more stable and rated "No."



NOTE: Figures 12 & 13

THERMAL EXPOSURE

1650°F 4 Hours Plus
1250°F 48 Hours

Letters Designate Individual Heats of Materials as Listed in Table 5

Figure 12. Effect of Alloy Element Concentrations on the Transformation Tendency of 10 Heats of Solution Annealed (2250°F, 2 Hours, Air Cooled) Stellite 6B During Thermal Exposure

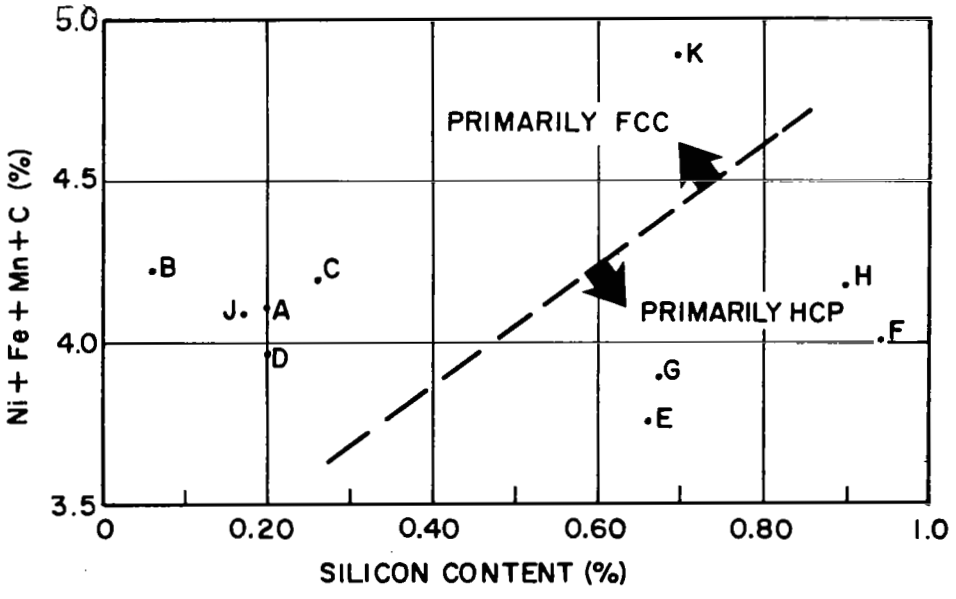


Figure 13. Effect of Silicon vs FCC Forming Elements on the Transformation Tendency of 10 Heats of Solution Annealed (2250°F, 2 Hours, Air Cooled) Stellite 6B During Thermal Exposure

It was shown previously that silicon has an influence on the embrittlement of L-605 (cobalt base alloy containing 20% Cr; 10% Ni; 15% W), Reference 3, due to elevated temperature exposure. The embrittlement of L-605 has been attributed to the precipitation of a Co_2W laves phase which is stabilized by the silicon in the alloy. Heats of L-605 with low silicon content show a decreased rate of becoming embrittled and metallographically exhibit less laves phase in the structure.

Metallographic examination, microprobe analysis, and X-ray diffraction of electrolytic extractions performed on thermally hardened and HCP transformed Stellite 6B revealed no evidence of laves phase. However, precipitates of such small size that they could not be detected by optical microscopy or X-ray diffraction have been detected by through transmission electron microscopy in other Co base alloys (see References 4 and 5). Such precipitates could be present in the hardened Stellite 6B and could be correlated with the matrix crystal structure transformation which also occurs. Therefore, to determine if silicon had a similar effect in the hardening and transformation of Stellite 6B as it has with the embrittlement L-605, the concentration of silicon in each of the ten heats was compared to the sum of the FCC stabilizers (see Figure 13). An even more distinct separation into two groups appears probable. Those heats with high silicon content and relatively low FCC stabilizer content appeared to have transformed more readily to HCP than heats with a low silicon content or with a high silicon content but also a high FCC stabilizer content.

The exact FCC stabilizing mechanism implied by these correlations is not known. In multiple constituent alloys many mechanisms can occur concurrently and/or sequentially. In the Co-W-C system, for instance, it has been postulated that nine individual reaction steps proceeding at different rates may occur in the transformation from the FCC to the HCP structure. These include various forms of martensitic precipitation, peritectoid, eutectoid and solutioning reaction mechanisms all reducing the free energy of the alloy and producing the final thermodynamically stable structure at a specific temperature (see Reference 6). No attempt was made in the present study to investigate

specific mechanisms. However, it does appear hopeful from the interim thermal exposure/structure correlations with chemical composition, that close control of the Stellite 6B alloy chemistry within the allowable composition range coupled with suitable processing techniques will provide an alloy with metallurgical stability at elevated temperature.

VI. CONCLUSIONS

The following conclusions were reached as a result of the various investigations:

Conventionally annealed Stellite 6B exhibits metallurgical instability when exposed at temperatures between 700° and 1550°F.

Thermal exposures in the temperature range 700 to 1550°F cause an increase in hardness of the alloy; a tendency toward transformation of the matrix from a FCC to a HCP crystal structure; and transformation of the M_7C_3 carbide islands normally present in the annealed microstructure to $M_{23}C_6$.

The thermally produced crystallographic transformation of Stellite 6B from FCC to HCP results in an average linear contraction of 0.092%; however, an unexplained large standard deviation, ± 0.0[illegible], was noted.

The elevated temperature reaction in Stellite 6B severely reduces the ductility and impact properties but the tensile strength of the material is not detrimentally affected.

Alloy chemistry control and a sufficiently rapid cool, produced by salt bath quenching, after solution annealing are two potential methods of stabilizing Stellite 6B, at least up to 1065°F, against the adverse elevated temperature reactions.

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APPENDIX A

CALCULATION OF PROPERTIES BASED ON DYNAMIC TEST DATA

ELASTIC MODULUS FROM RESONANCE IN THE TRANSVERSE MODE

$$E = .004160 \left(\frac{P}{L}\right)\left(\frac{L}{d}\right)^4 (F_1^t)^2 K^t$$

where: E = Dynamic elastic modulus
P = Weight of specimen in pounds
L = Length of specimen in inches
d = Diameter of specimen in inches
F_1^t = Transverse fundamental resonance frequency (Hz)

$$K^t = 1 + \left(\frac{d}{L}\right)^2 \left(3.092 + 0.854 \frac{E}{G}\right) - \left(\frac{d}{L}\right)^4 2.172 \frac{E}{G}$$

K^t is a correction factor for geometry and Poisson's ratio. The ratio $\frac{E}{G}$, where G is the dynamic modulus of rigidity, was determined for this purpose by the following:

$$\frac{E}{G} = K^L \left(\frac{F_1^L}{F_1^T}\right)^2$$

where: K^L is a correction factor (see below)

F_1^L = Longitudinal fundamental resonance frequency (Hz) at room temperature

F_1^T = Torsional fundamental resonance frequency (Hz) at room temperature

ELASTIC MODULUS FROM RESONANCE IN THE LONGITUDINAL MODE

$$E = .013190 \left(\frac{PL}{d^2}\right)\left(F_1^L\right)^2 K^L$$

where: F_1^L = Longitudinal fundamental resonance frequency (Hz)

$$K^L = 1 + \left(\frac{d}{L}\right)^2 (1.2337)\ \mu^2$$